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PATENT SPECIFICATION

L153.815



NO DRAWINGS

L153.815

Date of Application and filing Complete Specification: 14 July, 1967.

No. 32544/67.

Application made in Germany (No. F49751 IVd/12p) on 21 July, 1966.

Complete Specification Published: 29 May, 1969.

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Index at acceptance:—C2 C(3A14B3A, 3A14B8C, 3A14C3, 3A14C8C, 3A12A4A, 3A12B7, 3A12C5, 3A12B5, 1E6K4, KA22Y, KA220, KA227, KA30Y, KA34Y, KA340, KA577, KA627, KA71Y, KD20Y, KD30Y, KD34Y, KD341, KD578, KD626, KD727, MD173, MD186, MD215, MD247, MD25Y, MD250, MD252, MD276, MD30Y, MD305, MD326, MD351, MD352, MD656, 173—186—276, MH173, MH186, MH199, MH215, MH22Y, MH221, MH225, MH226, MH247, MH25Y, MH250, MH252, MH272, MH276, MH30Y, MH305, MH349, MH351, MH352, MH36Y, MH364, MH366, MH368, MH632, MH642, MH704, MH714, 173—186—276, 173—199—272)

Int. Cl.:—C 07 d 47/00

COMPLETE SPECIFICATION

Aliphatically Substituted Uretidiones

ERRATUM

SPECIFICATION NO. 1,153,815

Page 1, for Index at Acceptance C2C only read:—

(1E6K4, 3A12A4A, 3A12B5, 3A12B7, 3A12C5, 3A14B3A, 3A14B8C, 3A14C3, 3A14C8C, 20Y, 215, 22Y, 220, 221, 225, 226, 227, 247, 25Y, 250, 252, 30Y, 305, 326, 34Y, 340, 341, 349, 351, 352, 36Y, 364, 366, 368, 577, 578, 626, 627, 632, 642, 656, 704, 71Y, 714, 727, 173 - 186 - 276, 173 - 199 - 272, KA, KD, MD, MH)

THE PATENT OFFICE,  
30th December 1969

D 120681/4

- 20 hydrogen halide or diazabicyclo-(2,2,2)-octane, terminating the reaction when from 5 to 50% of the starting materials have reacted, and then isolating the resulting 1,3-diazacyclo-2,4-butanedione from the reaction mixture. 20
- Alternatively the reaction may be effected by thermally dimerising the aliphatic diisocyanate at 120° to 180°C, terminating the reaction when from 5 to 50% of the starting materials have reacted and isolating the resulting 1,3-diazacyclo-2,4-butanedione. The unreacted aliphatic isocyanates can be recovered from the reaction mixture and re-used. 25
- 30 Suitable starting materials for the process according to the invention include all aliphatic mono- and polyisocyanates. Where di- or polyisocyanates are used, uretidiones containing free isocyanate groups can be obtained. Suitable isocyanates include methyl isocyanate, ethyl isocyanate, propyl isocyanate, n-butyl isocyanate, isohexyl isocyanate, dodecyl isocyanate, oleyl isocyanate, stearyl isocyanate, cyclohexyl isocyanate, 2-chloro-ethyl isocyanate, 2-cyanoethyl isocyanate, 6-chlorohexyl isocyanate, ethylisocyanatoacetate, propyloxy propyl isocyanate, benzyl isocyanate, phenylethyl isocyanate, 1,2-ethylene diisocyanate, 1,4-tetramethylene-diisocyanate, 1,6-hexamethylene diisocyanate, 1,4- and 1,3-xylylene diisocyanate- $\omega,\omega$ , dipropylether- $\omega,\omega'$ -diisocyanate,  $\omega,\omega'$ -diisocyanato-1,4-diethyl benzene, 1,4-diisocyanatocyclohexane, 1-isocyanato-3-(isocyanato-
- 35

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Int. Cl.:—C 07 d 47/00

## COMPLETE SPECIFICATION

### Aliphatically Substituted Uretidiones

We, FARBENFABRIKEN BAYER AKTIENGESELLSCHAFT, a body corporate organised under the laws of Germany of Leverkusen, Germany, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

5 The present invention relates to aliphatically substituted uretidiones and to a process for their preparation. 5

10 Aromatically substituted uretidiones (1,3-diazacyclo-2,4-butanediones) and their preparation by the dimerisation of isocyanates using suitable catalysts, are already known. Aliphatically substituted uretidiones, i.e. dimers of aliphatic isocyanates, have not yet been produced. According to literature references, these compounds are totally unstable. Attempts to dimerise aliphatic isocyanates have always resulted in the formation of the trimerisation product. Attention is drawn in this connection to "Chemical Reviews" 57 (1957), page 55, and to Saunders and Frisch (Polyurethanes I), Interscience Publishers (1962, page 91). 10

15 We have now found a process whereby substituted uretidiones (1,3-diazacyclo-2,4-butanediones) can be prepared. We have found that aliphatically substituted 1,3-diazacyclo-2,4-butanediones can be obtained by dimerising aliphatic isocyanates in an inert organic solvent. This reaction may be carried out at 0°—180°C in the presence of a catalyst which is a tertiary phosphine, boron trifluoride or an adduct thereof, hydrogen halide or diazabicyclo-(2,2,2)-octane, terminating the reaction when from 5 to 50% of the starting materials have reacted, and then isolating the resulting 1,3-diazacyclo-2,4-butanedione from the reaction mixture. 20

25 Alternatively the reaction may be effected by thermally dimerising the aliphatic diisocyanate at 120° to 180°C, terminating the reaction when from 5 to 50% of the starting materials have reacted and isolating the resulting 1,3-diazacyclo-2,4-butanedione. The unreacted aliphatic isocyanates can be recovered from the reaction mixture and re-used. 25

30 Suitable starting materials for the process according to the invention include all aliphatic mono- and polyisocyanates. Where di- or polyisocyanates are used, uretidiones containing free isocyanate groups can be obtained. Suitable isocyanates include methyl isocyanate, ethyl isocyanate, propyl isocyanate, n-butyl isocyanate, isohexyl isocyanate, dodecyl isocyanate, oleyl isocyanate, stearyl isocyanate, cyclohexyl isocyanate, 2-chloroethyl isocyanate, 2-cyanoethyl isocyanate, 6-chlorohexyl isocyanate, ethylisocyanatoacetate, propyloxy propyl isocyanate, benzyl isocyanate, phenylethyl isocyanate, 1,2-ethylene diisocyanate, 1,4-tetramethylene-diisocyanate, 1,6-hexamethylene diisocyanate, 1,4- and 1,3-xylylene diisocyanate- $\omega,\omega$ , dipropylether- $\omega,\omega'$ -diisocyanate,  $\omega,\omega'$ -diisocyanato-1,4-diethyl benzene, 1,4-diisocyanatocyclohexane, 1-isocyanato-3-(isocyanato- 35

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methyl)-3,5,5-trimethylcyclohexane, 2,2,4-trimethylhexamethylene, 6-diisocyanate, 2,4,4-trimethylhexamethylene-1,6-diisocyanate, and 1,6,11-triisocyanatoundecane. Other aliphatic isocyanates are described in *Annalen* 562, pages 122 *et seq.*

5 The reaction can also be used with aliphatically bonded isocyanate groups in pre-polymers which are obtained from aliphatic polyisocyanates by partial reaction with water, alcohols, amines or carboxylic acids. Unfortunately, uretidiones of this kind are difficult, or even impossible to separate and purify. 5

10 The mono- and polyisocyanates can be used either individually or in admixture with one another. In order to restrict the formation of secondary products, the starting materials should be distilled *in vacuo* in the absence of atmospheric moisture, because all isocyanates contain dissolved carbon dioxide in varying quantities as a result of contact with traces of moisture. This purification is particularly advisable when tertiary phosphines are used as catalysts and when the reaction is carried out at temperature below 100°C. Where di- or polyisocyanates are used, uretidiones containing two or 15 more uretidione rings in the molecule can also be formed. Unfortunately, compounds such as these are extremely difficult to isolate in pure form. 15

The uretidiones according to the invention are compounds which correspond to the general formula



20 In this formula, R represents an aliphatic hydrocarbon radical. The radicals may be the same or different. In particular, R represents a linear or branched alkyl radical, preferably an alkyl radical containing 1 to 6 carbon atoms, or an alkenyl radical preferably with 3 to 6 carbon atoms. The radicals R may also be substituted. Examples of suitable substituents are NCO groups, halogens such as chlorine, nitrile groups, as 25 well as alkoxy, carbalkoxy and dialkylamine radicals, and aromatic radicals such as phenyl and naphthyl. 25

The catalysts for use when the compounds according to the invention are produced at 0 to 180°C are tertiary phosphines containing at least one aliphatic substituent, for example trialkyl phosphine, tributyl phosphine, phenyl dimethyl phosphine, as well as boron trifluoride and its adducts or etherates. One may also use dry hydrogen halide 30 gas or diazabicyclo-(2,2,2)-octane. 30

35 In order to carry out the process according to the invention, the reaction must be stopped at a very early stage, long before all the isocyanate has taken part in the reaction because otherwise an undesirably large amount of isocyanurate structures would be formed. For this reason, the reaction should be stopped after only 5 to 50% by weight of the starting materials have reacted, and any unreacted isocyanate should be separated off and returned to the reaction in another batch. The advantage of such a procedure is shown in the experimental data given in Example 2. The yield of separable diethyluretidione formed during the polymerisation of ethyl isocyanate using phosphines as catalysts, is still as large as 35%, when 37% of the reactants have been 40 used up at cessation of the reaction, but the yield drops to 17% at a conversion rate of 77%. 40

45 The reaction temperature varies according to the type of catalyst used. Boron trifluoride is preferably used at room temperature or at temperatures of up to 50°C. because the solubility of this catalyst in the reaction mixture decreases with rising temperature more quickly than the reaction velocity increases. For tertiary aliphatic or mixed aliphatic-aromatic phosphines, the optimum temperature lies in the range from 50 to 80°C. at which temperatures the uretidione component yield is at its maximum. Nevertheless, it would also be possible to use higher or lower temperatures because 50 uretidiones can be formed in fairly large quantities between 0 and 120°C. Apart from isocyanurates, other secondary products such as alkyl iminodialkylloxadiazinediones, carbodiimides and uretoneimines, are formed in increasing quantities at elevated temperature and, above all, on prolonged exposure to temperature coupled with low catalyst concentrations. Temperatures in the range from 120 to 150°C. are the most 55 favourable for thermal dimerisation in the absence of catalysts. At lower temperatures, adjustment of the equilibrium takes too long whilst at elevated temperatures, the uretidione is largely converted into the isocyanurate. 55

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The amount of catalyst required varies according to the nature and purity of the isocyanate used and according to the temperature applied. Quantities of from 0.1 to 5% by weight, based on the amount of isocyanate used, are generally sufficient in cases where tertiary aliphatic phosphines are used. The preferred quantity is between 0.3 and 2.0%. Boron trifluoride is used in a quantity of from 1 to 10%, by weight based on the amount of isocyanate preferably in a quantity of from 2 to 5%. The same applies as regards the quantity of polarising agents (for example hydrochloric acid) optionally used for thermal dimerisation. Diazabicyclo-(2,2,2)-octane is highly effective when used in quantities of 1 to 2% at temperatures from 120 to 150°C.

The reaction may be carried out in polar solvents such as esters, chlorinated hydrocarbons, ethers and ketones, or in the absence of solvents. The reaction is preferably carried out in the absence of solvents because the uretidiones formed are usually liquids, and excess isocyanate itself acts as a polar solvent.

To stop the reaction, conventional terminators, i.e. alkylating agents such as dimethyl sulphate or methyl toluene sulphonate, or acylating agents such as benzoyl chloride and carbamic acid chlorides, which prevent further reaction by "claiming" the pair of catalytically active, free electrons on the phosphorus, are used in the case of phosphines. The application of an elevated temperature of up to 80°C. also accelerates termination. The simplest way of removing boron trifluoride as catalyst is to apply a vacuum and increase the temperature.

The reaction mixture is preferably worked up by vacuum distillation. Since the boiling points of the monomers, dimers and polymers are usually far apart from one another, fractionation through columns is usually unnecessary and need only be applied in cases where it is intended to obtain the uretidiones in particularly pure form.

In order to minimise uretidione losses during the working-up, the temperature should be kept as low as possible. In the case of normal distillation, therefore, the quantities used should be small, whilst the temperature at the bottom of the column should not exceed 100°C.

Different methods of separation have to be used for higher boiling mono- and polyisocyanates. Thus, the monomer can be separated from the polymer component, for example, by thin-layer or falling-film distillation *in vacuo*, in which case the uretidiones are only briefly heated. The uretidiones can then be separated from the fairly high molecular weight secondary products by extraction with suitable petroleum ether fractions or benzene hydrocarbons, or by molecular distillation. In special cases, different distillation-extraction combinations are preferred.

The aliphatic uretidiones are mainly colourless at room temperature, are often readily labile and are rather oily liquids which do not have the pungent odour of monomeric isocyanates. They can be identified by analysis of molecular weight and above all by their infra-red spectrum which shows characteristic absorptions at 5.65—5.70  $\mu$ , 7.12—7.18  $\mu$  and 12.6—12.75  $\mu$ . Their structures were established by a series of characteristic reactions.

The aliphatic uretidiones may be used as intermediates in the production of plant protection agents and, in particular, if they still contain free isocyanate groups, as intermediate products in the production of plastics, lacquers and foams. They are of particular value because they are physiologically harmless by virtue of their low vapour pressure and because the isocyanate groups attached to the uretidione ring may be liberated by the application of elevated temperatures. Uretidiones which do not contain free isocyanate groups can be regarded as masked isocyanates.

In order that the invention may be more fully understood the following Examples are given by way of illustration only in which the parts and percentages are by weight:—

#### EXAMPLE 1

657 parts of n-butyl isocyanate which had been freshly purified by distillation were stirred with 9.85 parts of tri-n-butyl phosphine (1.5%) at 60°C. for 4 hours when the reaction was terminated at an NCO-value of 35.6% by the addition of 6.3 g of dimethyl sulphate, and by brief heating to 80°C. The conversion rate obtained amounted to 16.5%. The reaction mixture was then fractionated through a small column at 1.2 mm Hg. 546 parts (83.5%) of butyl isocyanate were recovered in a cold trap. Further fractions obtained were:

First runnings	3.6 parts	B.p. 45—92°C
Uretidione	49.0 parts	92—93°C yield 44% based on polymer
Intermediate runnings	1.9 parts	94—154°C
Isocyanurate	40.7 parts	155—158°C
Residual	13.0 parts	

5 The molecular weight of the dibutyl uretidione was found to be 200/201 (theoretical 198). Its infra-red spectrum showed characteristic bands at 5.68—7.16 and 12.75  $\mu$ . Elementary analysis C: 50.6/50.8 (calc. 50.7) H: 7.2/7.4 (calc. 7.1) N: 19.4/19.4 (calc. 19.7) O: 23.0/22.8 (calc. 22.5). 5

#### EXAMPLE 2

10 3 parts of tri-n-butyl phosphine were added to separate batches of 100 parts of freshly distilled ethyl isocyanate, and the mixture was stirred at room temperature until the required NCO-content was obtained. The reaction was then terminated by the addition of 2.4 parts of dimethyl sulphate to each batch, followed by one hour's heating to 60°C. The respective batches were then fractionated by vacuum distillation in a Widmer column. 10

15 Batch a): —reaction stopped after 8 hours at an NCO-value of 40.3%.  
Batch b): Reaction stopped after 70 hours at an NCO-value of 22.7%.  
Batch c): Reaction stopped after 168 hours at an NCO-value of 12.5%. 15

Distillation at 14 mm Hg reveals the following composition of the batches:

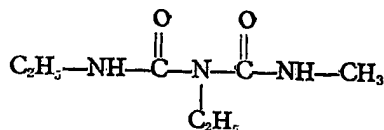
	Batch		
	a parts	b parts	c parts
First runnings up to 73°C	2.3	1.2	4.8
Uretidione 73—74°	12.8	19.4	13.1
Intermediate runnings	1.6	6.4	3.4
Isocyanurate 140—142°C	12.5	28.0	47.6
Residue	7.3	7.2	8.0
Total polymer	36.5	62.2	76.9
Isocyanurate recovered	63.4	37.4	22.9
Input	99.9	99.6	99.8
Uretidione yield based on polymer	35%	31.2%	17.1%
Conversion of isocyanurate	37%	62%	77%
Ratio of isocyanurate to uretidione	0.98	1.45	3.63

20 As this comparison of the three batches shows, high uretidione yields can only be obtained at low conversion rates because otherwise the isocyanurate component would be excessively increased. 20

The diethyl uretidione was a colourless liquid of  $Bp_{2.5} = 47-48^{\circ}\text{C}$ ,  $B.p._{14} = 74^{\circ}\text{C}$ . The molecular weight was found to be 143/143 (calc. 142). The infra-red spectrum showed the characteristic bands at 5.68, 7.18 and 12.75  $\mu$ .

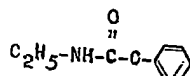
In order to confirm the structure of the diethyl uretidione the following reactions were carried out:

a) An excess of at least 1.7 parts of dry methylamine were reacted with stirring at  $0-10^{\circ}\text{C}$ . with 7.1 parts of diethyl uretidione. The diethylmethylbiuret of the following structure



was obtained in quantitative yield. ( $B.p._{0.5} = 120^{\circ}\text{C}$ ), molecular weight 173 (calc. 173). Elementary analysis C: 48.7% (calc. 48.6), H: 8.9% (calc. 8.7), N: 24.4% (calc. 24.3), O: 18.2% (calc. 18.5). The infra-red spectrum showed absorptions which were characteristic for biuret carbonyl groups at 5.92 and 6.9  $\mu$ .

b) 7.1 parts of the diethyl uretidione were heated with 47 parts of phenol with stirring for 3 hours at a temperature of up to  $120^{\circ}\text{C}$ . After removing excess phenol by distillation N-ethylcarbamic acid phenyl-ester of the following structure



was obtained in a quantitative yield ( $B.p._{0.6} = 96-100^{\circ}\text{C}$ ), molecular weight 169 (calc. 165). Elementary analysis C: 65.9% (calc. 65.4), H: 7.1% (calc. 6.7), N: 8.2% (calc. 8.5), O: 19.3 (calc. 19.4). The infra-red spectrum showed an absorption at 5.82  $\mu$  which was characteristic for the urethane carbonyl group.

#### EXAMPLE 3

1 part of triethylphosphine was added to 280 parts of allyl isocyanate. The mixture was stirred at room temperature. After 75 minutes the reaction was terminated at an NCO-value of 32.9% by addition of 1 part dimethyl sulphate and briefly heating to  $70^{\circ}\text{C}$ . By distillation in vacuum in a Widmer-column the following fractions were obtained:

- 195 parts unreacted allyl isocyanate
- 34 parts diallyl uretidione ( $B.p._{1.0} = 66^{\circ}\text{C}$ )
- 5 parts intermediate runnings ( $B.p._{1.0} = 66-136^{\circ}\text{C}$ )
- 35 parts triallyl isocyanurate ( $B.p._{1.0} = 136-140^{\circ}\text{C}$ ) and
- 11 parts residue.

The uretidione was a colourless liquid. Molecular weight 163 (calc. 166): elementary analysis C: 57.9% (calc. 57.9), H: 6.2% (calc. 6.0), N: 16.9% (calc. 16.9), O: 19.1% (calc. 19.3). The IR-spectrum shows, besides the carbonyl frequency at 5.62  $\mu$  which is characteristic for uretidiones, strong absorptions only at 6.94 and 7.20-7.55-10.75 and 12.70  $\mu$ .

#### EXAMPLE 4

0.3 parts of tri-n-butylphosphine were added to 100 parts of methoxy methyl isocyanate (isocyanatomethyl methylether) (NCO-content 48.3%) which was freshly purified by distillation. An exothermic reaction took place which could only be controlled by cooling. After 15 minutes the reaction was terminated by addition of 0.2 parts of dimethyl sulphate and heating to  $70^{\circ}\text{C}$ . The reaction mixture showed an NCO-content of 31.5% and could be separated by vacuum distillation in a Widmer-column into the following constituents:

- 54 parts of starting material obtained by condensing in a cooling bath
- 18 parts of dimethoxy methyl uretidione ( $B.p._{1.0} = 86^{\circ}\text{C}$ ) which crystallised out (melting point  $69^{\circ}\text{C}$ )
- 25 parts of residue, mainly consisting of trimethoxy methyl isocyanurate, which crystallises out over a longer period.

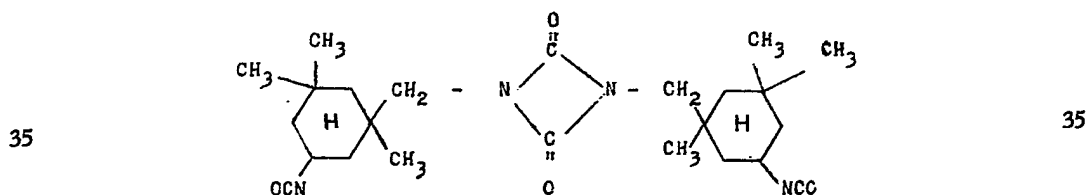
The raw uretidione could be sublimed in vacuum. By this means 15 to 16 parts of the pure product (melting point 73°C) are obtained. Molecular weight 170 (calc. 174), methoxy group analysis according to the method of Zeisel: 35.5% (calc. 35.6%). Elementary analysis C: 41.6% (calc. 41.4), H: 5.9% (calc. 5.8), N: 16.1% (calc. 16.1), O: 37.1% (calc. 36.8). Besides the absorption for the uretidione carbonyl group at 5.6  $\mu$  and the band for the ring oscillation at 7.07  $\mu$ , characteristic absorptions at 7.48—8.20—8.65—9.25—10.55—11.08—12.70  $\mu$  were observable in the IR-spectrum.

#### EXAMPLE 5

Over the course of 15 minutes, 12 parts of gaseous boron trifluoride were introduced into 130 parts of 6-chlorohexyl isocyanate. In a slightly exothermic reaction the temperature rose over the course of 2 hours, to 30°C, and the NCO-content dropped from 26.1% to 20.5%. The catalyst was removed from the reaction mixture by heating to 70°C. under vacuum and the reaction mixture was subsequently filtered in order to remove small amounts of solid impurities. Subsequently unreacted 6-chlorohexyl isocyanate was removed by repeated thin-layer-distillation at 0.3 mm Hg. and 135°C. In this way 104 parts of unchanged 6-chlorohexyl isocyanate were regained. 24 parts of a brown yellow viscous liquid were obtained, more than 2/3 of which consisted of bis-6-chlorohexyl uretidione. The main impurity was found to be the corresponding isocyanurate observed by means of its IR-spectrum with absorptions at 5.66—5.93 and 7.13  $\mu$ . Molecular weight 398.

#### EXAMPLE 6

240 parts of 5-isocyanatomethyl-3,3,5-trimethylcyclohexyl isocyanate were stirred together with 2.4 parts of tri-n-butyl-phosphine at room temperature until the NCO-content, over the course of 30 hours dropped from 37.8% to 33.6%. The reaction was subsequently stopped by addition of 1 part of dimethyl sulphate and 1 part p-toluene sulphonic acid methyl ester and heating to 80°C. for 1/2 hour. By thin-layer-distillation at 1 mm Hg and 150°C., 178 parts of the starting material are separated as a distillate. 15 parts of the uretidione crystallise out from the concentrate which is a viscous yellow liquid having an NCO-content of 21.0%. The crystals are filtered under suction with exclusion of moisture and are washed with petroleum ether, and have a melting point of 144°C. Besides the absorptions at 3.44—4.44—5.72—7.18  $\mu$  which are characteristic of aliphatic uretidiones containing isocyanate groups the IR-spectrum shows only traces of biuret as impurity. Molecular weight 476 (calc. 444); NCO-content 18.7% (calc. 18.9%). The following constitution



is most probable from the NMR-spectrum.

#### EXAMPLE 7

2090 parts of 1,6-hexamethylenediisocyanate were heated to 140°C. over the course of 8 hours. After this time the NCO-content of the dark reaction mixture dropped from 50.0 to 49.0%. In a subsequent continuous distillation process excess unreacted 1,6-hexamethylenediisocyanate was separated. After thin-layer-distillation at 1 mm Hg and 150°C., carried out 3 times, the following fractions were obtained:

1st distillation	632 parts concentrate and 1451 parts of distillate	
2nd distillation	272 parts concentrate and 356 parts of distillate	
3rd distillation	110 parts concentrate and 161 parts of distillate	
total	<u>1014</u> parts concentrate and <u>1968</u> parts of distillate	

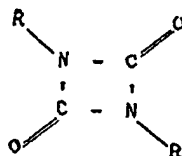
The concentrate mainly consist of uretidione of the 1,6-hexamethylenediisocyanate as may be seen from IR-spectrum. This uretidione, in its crude form, has an NCO-content of 24.6% (calc. 25.0%), and a molecular weight of 408 (calc. 336) and

contains, in addition to considerable quantities of isocyanurate and unknown impurities, only 0.2% of the monomer. By extraction with suitable aliphatic hydrocarbons which is described in the following procedure, pure uretidione, a colourless liquid, can be obtained from the crude product:

- 5 102 parts of the crude product were treated for 16 hours in a liquid-liquid-extractor with 1000 parts of iso-octane which was dried over sodium. The iso-octane solution was separated from the residue which contained in addition to higher molecular weight constituents, coloured impurities. The solvent was removed by distillation *in vacuo* from the iso-octane solution. 53 parts of pure uretidione were obtained, molecular weight 348. The IR-spectrum did not show any impurities, even in traces. In addition to the carbonyl frequency at 5.68  $\mu$ , the isocyanate band at 4.43  $\mu$  and the band for the uretidione ring oscillation at 7.18  $\mu$  only absorptions at 3.45—3.55—6.88—7.46 and 12.74  $\mu$  were to be seen in the IR-spectrum.

WHAT WE CLAIM IS:—

- 15 1. Aliphatically substituted 1,3 - diazacyclo - 2,4 - butanediones corresponding to the formula



in which the groups R represent aliphatic hydrocarbon radicals which may be the same or different and which may be substituted.

- 20 2. 1,3-diazacyclo-2,4-butanediones as claimed in claim 1 in which R is a linear or branched alkyl radical containing 1 to 6 carbon atoms or an alkenyl radical with 3 to 6 carbon atoms.
- 25 3. 1,3-diazacyclo-2,4-butanediones as claimed in claim 1 or claim 2 in which one or both the radicals R is substituted by an NCO group.
4. The compound dibutyl-uretidione.
5. The compound diethyl-uretidione.
6. A process for the production of an aliphatically substituted 1,3-diazacyclo-2,4-butanedione as claimed in claim 1 wherein an aliphatic diisocyanate is dimerised at a temperature of 0 to 120°C in the presence of a catalyst which is a tertiary phosphine with at least one aliphatic substituent, boron trifluoride or an adduct thereof, a hydrogen halide or diazabicyclo-(2,2,2)-octane, the reaction being terminated after the conversion rate has reached from 5% to 50%, and 1,3-diazacyclo-2,4-butanedione is isolated from the reaction mixture.
- 30 7. A process for the production of an aliphatically substituted 1,3-diazacyclo-2,4-butanedione as claimed in claim 1 wherein an aliphatic isocyanate is dimerised at a temperature of 120°C to 180°C, the reaction being terminated after the conversion rate has reached from 5% to 50%, and the 1,3-diazacyclo-2,4-butanedione is isolated from the reaction mixture.
- 35 8. A process as claimed in claim 6 or claim 7 when carried out in an inert organic solvent.
- 40 9. A process as claimed in any one of claims 6 to 8 wherein the reaction is terminated by addition of an alkylating or acylating agent.
10. A process as claimed in claim 9 wherein the reaction is terminated by application of a vacuum and removal of the catalyst at an increased temperature.
- 45 11. A process as claimed in any one of claim 6 or claims 8 to 10 wherein 0.1 to 5% by weight, based on the isocyanate, of tertiary phosphine catalyst is used.
12. A process as claimed in claims 8—10 wherein 1 to 10% by weight, based on the isocyanate, of boron trifluoride catalyst are used.
13. A process as claimed in any one of claims 7 to 10 when carried out at a temperature of 120 to 150°C.
- 50 14. A process for the production of aliphatically substituted 1,3-diazacyclo-2,4-butanediones substantially as herein described with reference to the Examples 1 to 6.
15. A process for the production of aliphatically substituted 1,3-diazacyclo-2,4-butanediones substantially as herein described with reference to Example 7.
- 55 16. 1,3-diazacyclo-2,4-butanediones when produced by the process claimed in any of claims 6 to 15.



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